DER MATERIALS QUARTERLY PROGRESS REPORT

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For:

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January—March 2003

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Objective

The main objective of this program is to work with commercial materials suppliers (foil and thin sheet) and recuperator manufacturers to enable manufacture of upgraded recuperators from cost effective alloys with improved performance and temperature capability. The near term goal is better performance to or above 704°C (1300°F), and the longer-term goal is reliable performance at 760°C (1400°F) and higher.

Highlights

<u>Materials for use to about 704°C (1300°F)</u>
ORNL participated in a joint project with Allegheny-Ludlum Technical Center to modify commercial-scale processing to improve the creep-resistance of sheet and foils of standard 347 stainless steel at 700-750°C. Preliminary creep-rupture and microstuctural data on trial pieces of 10 mil sheet clearly indicated creep resistance at 700-750°C could be improved. This quarter, production quantities of 3.2 mil foil and 10 mil sheet of 347 steel were produced according to the specifications supplied by Ingersoll-Rand Energy Systems for their brazed plate and fin (BPF) recuperator. Creep testing at 704°C and 22 ksi indicates improvements in rupture life of 75% for the foil and 35% for sheet with the modified processing. Creep testing will continue at 750°C and product will be shipped next quarter. Similar processing of nominal amounts of 4 and 5 mil foils, applicable to other kinds of recuperators, will also continue next quarter.

<u>Materials for use at 760°C (1400°F) or higher</u>
Commercial 3 mil foil of HR120 from Elgiloy Specialty Metals (Elgin, IL) was obtained and creep-tested at 704°C/152 MPa and 750°C/100 MPa. The HR 120 foil lasted 900h at 704°C, and lasted for 3300 h at 750°C, both with good rupture ductility. The creep resistance at 750°C is about 13 times better than standard 347 steel foil with standard commercial processing.

Technical Progress

Recuperator Component Analysis

Several different microturbine OEMs have provided pieces of fresh and engine-tested PFR and PSR recuperators made from standard 347 stainless steel for analysis and testing and characterization is nearly complete. These components are manufactured from coils of standard, commercial 347 steel that range from 3-4 mil foil to up to 10 mil sheet, and include the additional manufacturing steps of welding and/or brazing. ORNL is characterizing the engine-tested components and measuring the changes relative to fresh (as-manufactured) components. Detailed component analysis will be reported to each OEM, and will be used to help define specific advanced material solutions tailored to achieving better performance and temperature capability for the various kinds of recuperators.

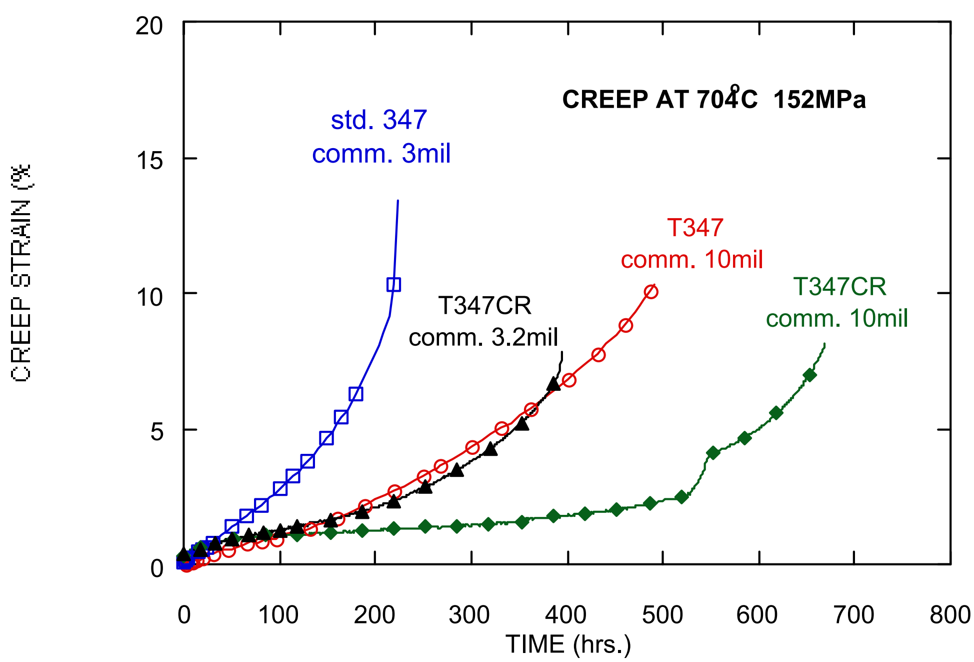

Figure 1. ORNL creep rupture testing of standard 347 steel foils (3-3.2 mils)and sheet (10 mils) at 704°C, comparing standard and modified commercial processing conditions. This is a joint project with ORNL and Allegheny-Ludlum Technical Center.

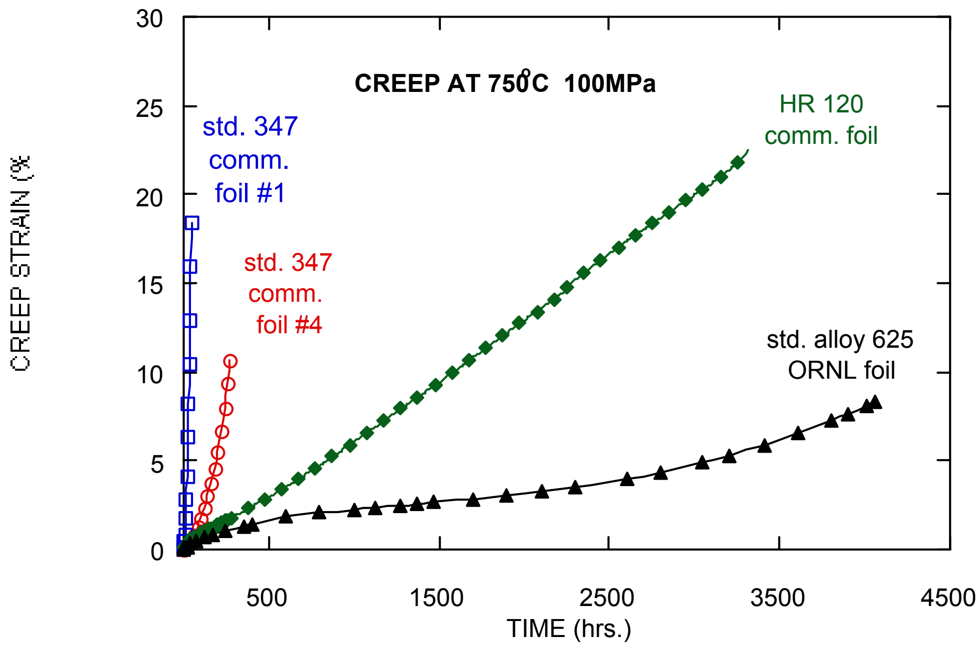

Figure 2. ORNL creep testing at 750°C of several standard commercial 347 stainless steel foils and sheet supplied by recuperator manufacturers, together with commercial HR120 foil provided by Elgiloy, and ORNL lab-scale processed foil of alloy 625.

Selection and Commercial Scale-Up of Advanced Recuperator Materials:
a) Materials for use to about 704°C (1300°F)

ORNL creep testing at 700-750°C to establish the baseline behavior for current recuperators made from standard 347 stainless steel has been completed. Creep testing at 704°C (1300°F) and 152 MPa, gave rupture lives ranging from 50 to 500 h, and testing at 750°C and 100 MPa gave rupture lives from 50 to 250 h.

ORNL initiated a joint project with Allegheny-Ludlum Technical Center in FY 2003 to modify processing to improve the creep-resistance of sheet and foils of standard 347 stainless steel at 700-750°C. The objective is to provide commercial materials that Ingersoll Rand and other recuperator manufacturers can use to produce recuperator components with improved creep-resistance at about 700°C or slightly above. Trial runs of 10 mil 347 steel sheet were creep tested at 704°C/152 MPa and 750°C/100 MPa. Preliminary data indicated clear changes in grain size distribution produced at least a 15-20% improvement in creep resistance.

This quarter, production quantities of 3.2 mil foil and 10 mil sheet of 347 steel were produced according to the specifications supplied by Ingersoll-Rand Energy Systems for their brazed plate and fin (BPF) recuperator. Creep testing at 704°C and 22 ksi indicates improvements of 75% for the foil and 35% for sheet in rupture life with the modified processing (Fig. 1). Creep testing will continue at 750°C and product will be shipped next quarter. Similar processing of nominal amounts of 4 and 5 mil foils, applicable to other kinds of recuperators, will also continue next quarter.

Oxidation testing of ORNL modified 347 steels continued at 650-800°C this quarter, and the data out to several thousand hours indicates severe effects of water vapor enhanced oxidation at 650ºC on standard 347 steel, but much better behavior of the new ORNL modified 347 steels, and the advanced alloys that include HR120, modified 803, NF709 and alloy 625. Oxidation testing will continue, and microstructural analysis of corrosion specimens tested at higher temperatures will continue.

<u>b) Materials for use at 760°C (1400°F) or higher</u>

HR 120 (Fe-25Cr-35Ni) is one of the more promising commercially available material with significantly better creep-resistance and corrosion-resistance in this temperature range at 3-4 times the cost of 347 stainless steel. Commercial 3 mil foil of HR120 has been obtained by ORNL from Elgiloy Specialty Metals (Elgin, IL) and has been creep-tested at 704°C/152 MPa and at 750°C/100 MPa. The HR 120 foil lasted 900h at 704°C, and lasted for 3300 h at 750°C, both with good rupture ductility. The creep resistance at 750°C is about 13 times better than standard 347 steel foil with standard commercial processing.

Status of Milestones

FY2003 – Produce standard 347 steel with modified commercial processing to maximize creep resistance for sheet and foil gages. Certify properties and provide sufficient creep-resistant 347 steel to microturbine OEMs to manufacture recuperators with improved performance for use at or slightly above 700°C (April 2003). On schedule.

Industry Interactions

Microturbine OEM Ingersoll-Rand Energy Systems has agreed to take standard 347 sheet and foils being processed by Allegheny-Ludlum and ORNL for improved creep resistance, and has supplied the specific details on sizes and widths required for recuperator manufacturing. Discussions with Capstone to define their interest in obtaining foils of standard 347 for recuperator manufacturing continue.

Problems Encountered

None

Publications/Presentations

Invention Disclosure on “Engineered Microstructures for Improved Heat Resistance of Stainless Steels and Alloys for Thin-Section/Foil Applications” by P. J. Maziasz, R. W. Swindeman, B. A. Pint, M.L. Santella and K.L. More was filed with ORNL on September 22, 2002. A U.S. Patent application based on this invention disclosure was developed and filed this quarter.

P. J. Maziasz, B. A. Pint, R. W. Swindeman, K. L. More and E. Lara-Curzio, “Selection, Development and Testing of Stainless Steels and Alloys for High Temperature Recuperator Applications,” paper GT2003-38762 was accepted for publication at the 2003 Turbo Expo.

Recuperator Alloys – Composition Optimization for Corrosion Resistance

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Objective

In order to provide a clear, fundamental understanding of alloy composition effects on corrosion resistance of stainless steel components used in recuperators, the oxidation behavior of model alloys is being studied. The first phase of this study narrowed the range of Cr and Ni contents required to minimize the accelerated corrosion attack caused by water vapor at 650°-800°C. Other factors that continue to be investigated include the effects of temperature, alloy grain size, phase composition and minor alloy additions. These composition and microstructure effects also will provide data for life-prediction models and may suggest a mechanistic explanation for the effect of water vapor on the oxidation of steels. This information will be used to select cost-effective alloys for higher temperature recuperators.

Highlights

Characterization of the chemical composition of Nb-modified Fe-20Cr-25Ni foil exposed for 6,000h at 800°C in humid air indicates that the Cr consumption rate was significantly higher than indicated by the mass change. At the same time the specimen mass began to rise, the average Cr content across the 100μm thick foil had dropped to <15wt%, suggesting that accelerated attack was beginning and that stainless steel foils are unlikely to have extended lifetimes at 800°C and that alumina-forming alloys are needed. In contrast, foil specimens exposed for 4,000 and 7,500h at 700° in humid air showed only modest Cr loss near the foil surface, suggesting that significantly longer lifetimes are possible at this temperature.

Technical Progress

Experimental Procedure

As outlined in previous reports, foils were rolled to 100μm (4mil) at ORNL by a combination of hot and cold rolling of commercial material and laboratory castings. Foils of Nb-modified Fe-20Cr-25Ni were rolled from commercial tubing (NF709). Model alloys were vacuum induction melted and cast in a water-chilled copper mold, followed by hot forging and rolling to 2.5mm. The sheets were then cold rolled to 1.25mm and annealed under Ar + 4%H_2 for 2 min at 1000°C. Oxidation foil specimens were tested in the as-rolled condition and sheet specimens were polished to 600 grit SiC. The oxidation tests were done in air + 4 vol.% and 10 vol.% water vapor with 100h cycles at 650°, 700° and 800°C.

Results for foils from commercial alloys

Figure 1 shows results for various foils during 100h cycles at 800°C. The mass gains are relatively low for these highly alloyed materials. In comparison, type 347 stainless steel typical showed a mass

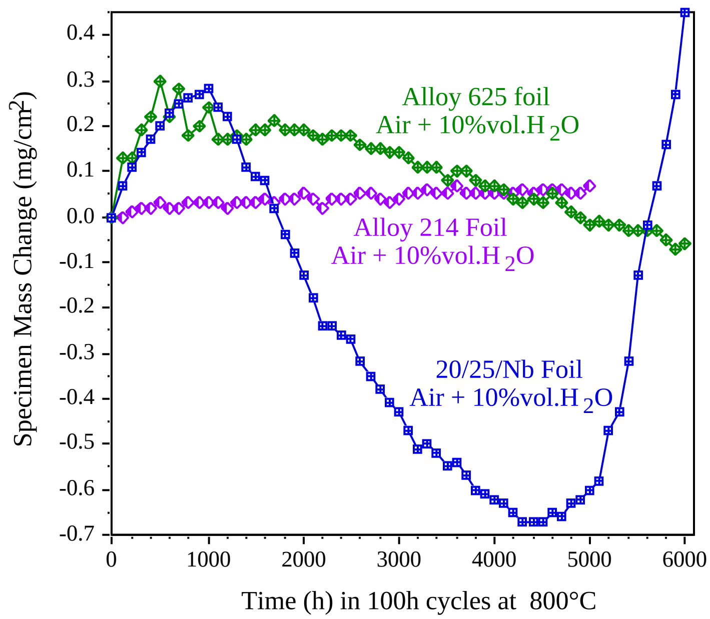

Figure 1. Mass change of various foils during 100h cycles at 800° in air plus 10% water vapor. The mass changes were relatively small for all of the alloys.

gain of over 4mg/cm^2 in less than 1000h in this test. The mass losses for alloy 625 (Ni-22Cr-9Mo-4Nb-3Fe) and 20/25Nb are attributed to the evaporation of the chromia scale. However, the mass gain for 20/25Nb suggested that accelerated attack might be beginning during the last 1,500h of the test. In contrast, alloy 214 (Ni-16Cr-4Al-3Fe) showed a low constant mass gain due to the formation of an alumina scale which is less affected by water vapor. The difference also is clear in cross-section where the scale on alloy 214 (Figure 2c) is much thinner than that on the chromia-forming foils. While thicker than the alumina scale, the chromia scales still appeared relatively thin and mostly

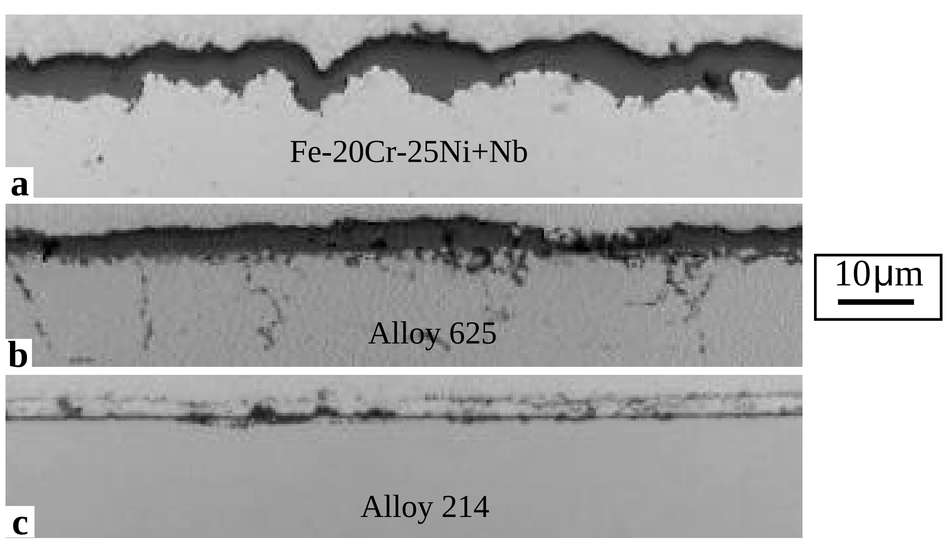

Figure 2. Light microscopy of polished cross-sections of the scale formed at 800°C in air + 10%H_2O on (a) Fe-20Cr-25Ni+Nb after 6,000h, (b) alloy 625 after 6,000h and (c) alloy 214 after 5,000h.

protective, although some internal attack was observed

To further investigate the attack on the 20/25Nb foil, electron probe microanalysis (EPMA) was used. Figure 3 shows a back-scattered electron image of the oxidized foil as in Figure 2a. The bright particles are rich in Nb relative to the substrate and the darker (gray) particles near the center are rich in Cr. In order to assess the amount of Cr loss, a Cr profile was taken diagonally across the foil. The

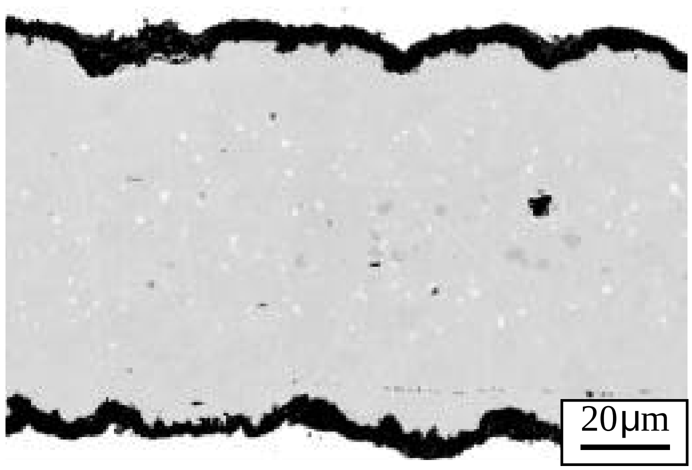

Figure 3. EPMA Cr profiles across Nb-modified Fe-20Cr-25Ni foil and plate specimens exposed in humid air for various times at 700° and 800°C. The 800°C exposure significantly reduced the Cr content in the alloy.

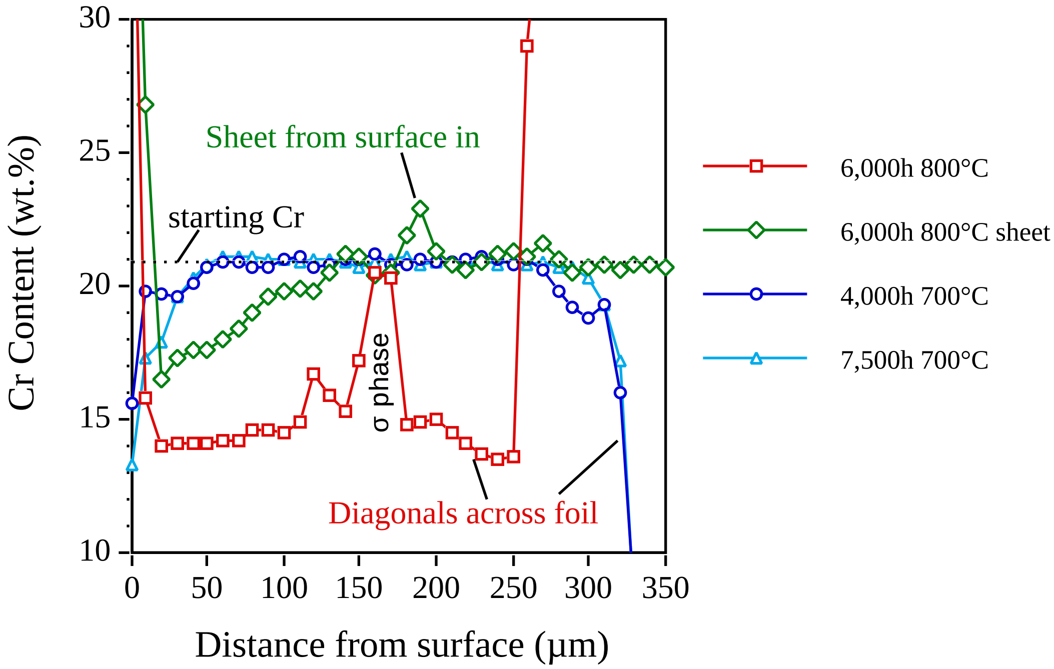

Figure 4. EPMA Cr profiles across Nb-modified Fe-20Cr-25Ni foil and sheet specimens exposed in humid air for various times at 700° (4%H_2O) and 800°C (10%H_2O). The 800°C exposure significantly reduced the Cr content in the alloy.

profile in Figure 4 shows that the Cr content has dropped to less than 15% after 6000h at 800°C. One spike in the Cr content is believed to correspond to a Cr-rich σ phase precipitate in the foil. For comparison to the foil profile, Cr profiles also were obtained from some additional specimens. One was a 1mm thick specimen that was tested for 6,000h at 800°C in the same test with the foil specimen. Near the surface of the sheet specimen, the Cr depletion was similar to the foil specimen. However, the depletion only lasted over a distance of about 120µm before the Cr level returned to the starting Cr content. More spallation (and thus more metal loss) was observed from the thicker specimen so it is somewhat difficult to compare it to the foil specimen where no spallation was observed.

Foils exposed at 700°C also were examined, Figure 4. In this case, the foils were exposed to air + 4vol.%H_2O for 4,000 and 7,500h. Very little depletion was observed in these specimens suggesting that much longer lives may be possible at 700°C.

<u>Results for sheet specimens of model alloys</u>
Along with commercial composition foils, testing of model austenitic alloys is continuing. The current series of model alloys focused on Cr contents of 16-20% and Ni contents of 15-20% and minor alloy additions of Mn, Si and La, which have shown the most promising beneficial effects. Testing has proceeded past 2,000h for the best compositions which contain Mn and Si, Figure 5. Testing of the leanest alloys, with 16Cr and 15Ni, has concluded because of accelerated attack in all cases. In these alloys, the additions did not prevent the onset of accelerated attack. The most promising composition is Fe-20Cr-20Ni with Mn and Si additions. At 650°, 700° and 800°C, this composition still shows low mass gains and no signs of accelerated attack. The specimens with 16Cr/20Ni and 20Cr/15Ni have begun to show accelerated attack at 800°C, Figure 5c, but not at the lower temperatures.

Status of Milestones

Draft a report summarizing results on the use of minor alloy additions to improve corrosion performance in exhaust gas environments. (January 2003) Completed - NACE Paper 03-499 (see below).

Industry Interactions

Discussed the oxidation performance of 347 and alloy 625 foils with Jim Rakowski from Allegheny Ludlum in March 2003.

Presented program results at the NACE Corrosion 2003 meeting in March where various industry representatives were present in the audience.

Problems Encountered

None.

Publications/Presentations

B. A. Pint and R. Peraldi, (2003) “The Effect of Alloy Composition on the Performance of Stainless Steels in Exhaust Gas Environments,” NACE Paper 03-499, Houston, TX, presented at NACE Corrosion 2003, San Diego, CA, March 2003.

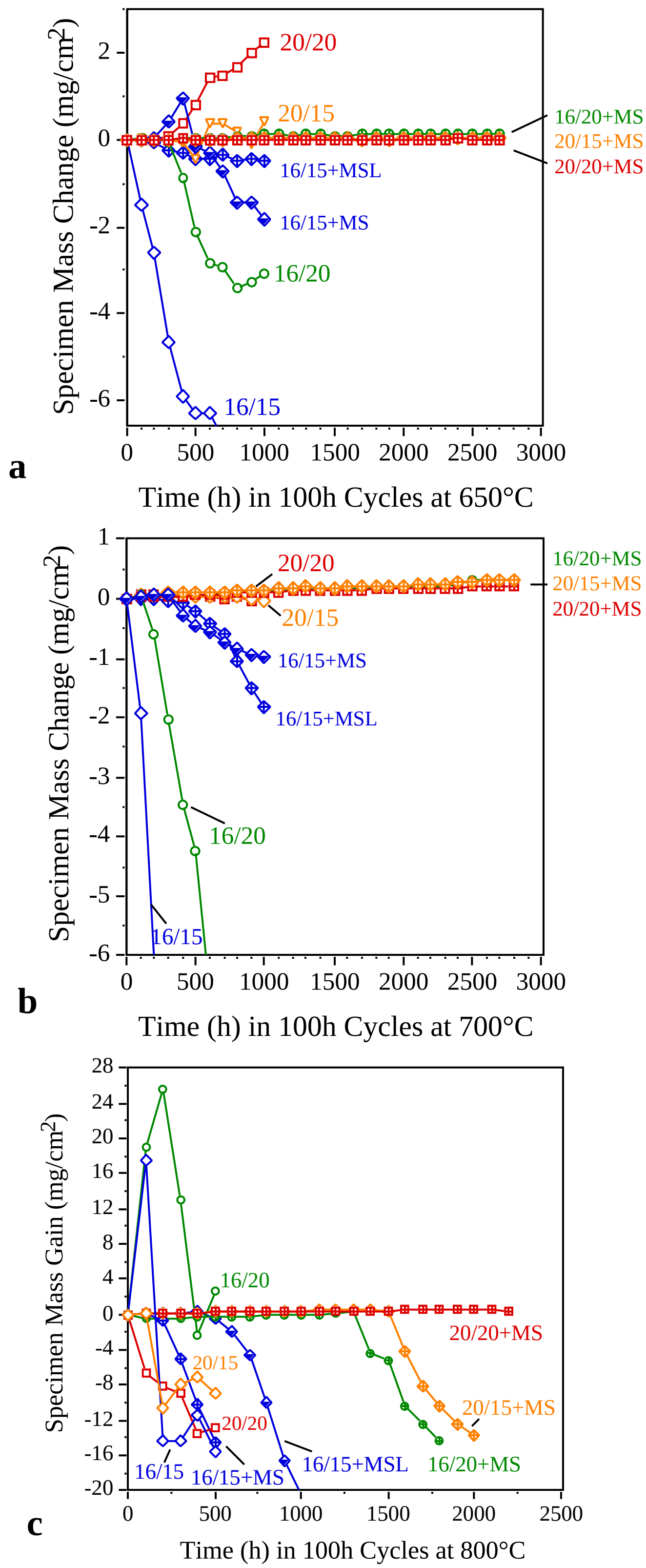

Figure 5. Specimen mass changes for rolled model Fe-Cr-Ni alloys (specified by their Cr/Ni contents) some of which contain Mn and Si (MS) or Mn, Si and La (MSL) during 100h cycles in air plus 10%H_2O at (a) 650°C, (b) 700°C and (c) 800°C.

Recuperator Materials Testing and Evaluation

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Objective

The objective of this sub-task is to screen and evaluate candidate materials for the next generation of advanced microturbine recuperators. To attain this objective, a commercially-available microturbine was acquired and in coordination and collaboration with its manufacturer, it was modified to operate at recuperator inlet temperatures as high as 843°C. The durability of candidate recuperator materials will be determined by placing test specimens at a location upstream of the recuperator, followed by determination of the evolution of the material's physical and mechanical properties as a function of time of exposure. During exposure tests inside the microturbine, it will be possible to subject test specimens to various levels of mechanical stress by using a specially-designed sample holder and pressurized air. The selection of materials to be evaluated in the modified microturbine will be made in coordination and collaboration with other tasks of this program and with manufacturers of microturbines and recuperators.

Highlights

Four recuperators for Parallon 75 microturbines were received from CANMET of Canada and are currently being sectioned for mechanical and microstructural evaluation.

Technical progress

An important objective of this task is to evaluate the evolution of mechanical and physical properties of microturbine recuperator materials as a function of service history. To accomplish this objective, microturbine recuperators that have been decommissioned after field operation are being evaluated to characterize their microstructure and to determine their residual mechanical and physical properties. During the reporting period, four recuperators for Parallon 75 microturbines were received from CANMET of Canada. Two of those recuperators were received embedded in microturbine frames and work is in progress to remove those two recuperators and to complete the sectioning and characterization of the other two. Figure 1 is a photograph of the identification tag of on of those recuperator while Figure 2 contains a series of photographs that illustrate some of the steps involved in the process that has been adopted for removing the recuperators from their casing and for sectioning the recuperator to obtain specimens for mechanical and microstructural characterization.

Figure 1. Plaque removed from recuperator .

Figure 2. Process to remove recuperator from casing using torch.

The removal of the recuperators from their casing has been achieved using torch cutting techniques. After the recuperators were removed from their casing, they were sectioned at three different locations along their length to investigate the mechanical properties as a function of position. Sections 1-inch thick were obtained, which corresponds to approximately six cells. Figure 3 illustrates the location of the transverse cuts while Figure 4 shows one of the 1-inch thick sections. From each section, strips 0.5-inch wide and as long as the height of the recuperator (approximately 9 inches) were cut using electric discharge machining, and each strip was further cut in half along their length to investigate the effect of location (up/down) on the mechanical properties of the material. In this particular recuperator design, hot exhaust gases enter through the bottom end exit from the top, while compressed air enters and exist through manifolds located at diagonally opposite locations as shown in Figure 2. Figure 5 shows a couple of strips used for tensile evaluation. The strip on the bottom had been cut in half and tested. Note in Figures 3 and 5 the change in coloration along the length of the strip and the corrugation pattern of the material.

The strips were evaluated under tension at a constant crosshead displacement rate at ambient conditions using an electromechanical testing machine equipped with hydraulic wedge grips and a clip-on extensometer.

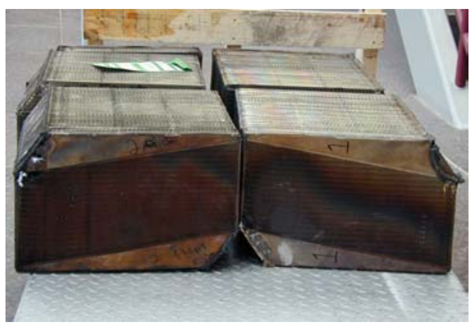

Figure 3. Sectioning of recuperators. Transverse cuts were performed along their length to obtain 1”-thick sections. Note the change in color along the height of the recuperator. Flat sections along the corner are connected to manifolds and correspond to inlet/outlet regions for compressed air.

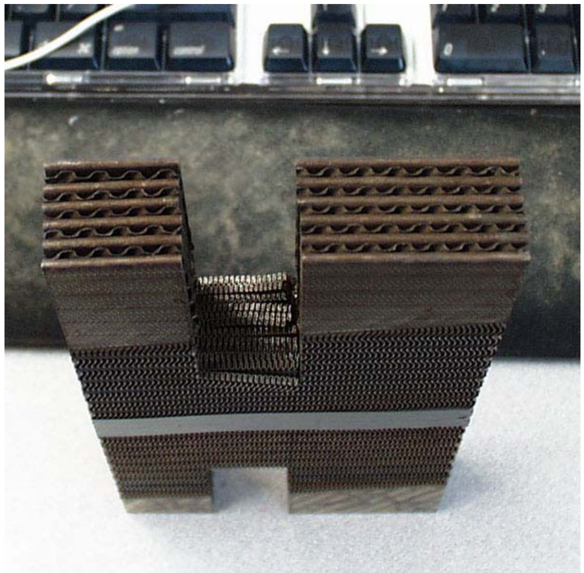

Figure 4. 1-inch thick section of recuperator containing approximately 6 cells.

Figure 5. Recuperator strips before (top) and after (bottom) tensile testing. The strip on the bottom had been cut into two pieces prior to testing.

Figure 6 shows a collection of load versus strain curves obtained from the tensile evaluation of recuperator strips. The shape of these curves is similar to those obtained previously from the evaluation of similar test specimens. The curves have a liner region associated with elastic behavior, a well-defined transition into a regime associated with plastic deformation, and increasing stiffness with strain, associated with the distortion of the corrugation geometry. Work is in progress to characterize the microstructure of these materials including the structure of the oxide layer.

During this reporting period work was also continued to evaluate and characterize materials exposed in ORNL's recuperator testing facility. The base line properties of alloys HR230, Haynes 214 and Haynes 230 were determined through the evaluation of miniature tensile specimens. Test specimens were obtained with the major axis either parallel or perpendicular to the rolling direction of the foil. Figure 7-9 show a series of photographs associated with the experimental set-up used to evaluate miniature tensile specimens. As indicated in previous reports, miniature tensile specimens will be obtained from sections of foils that have been exposed in ORNL's recuperator testing facility for various periods of time.

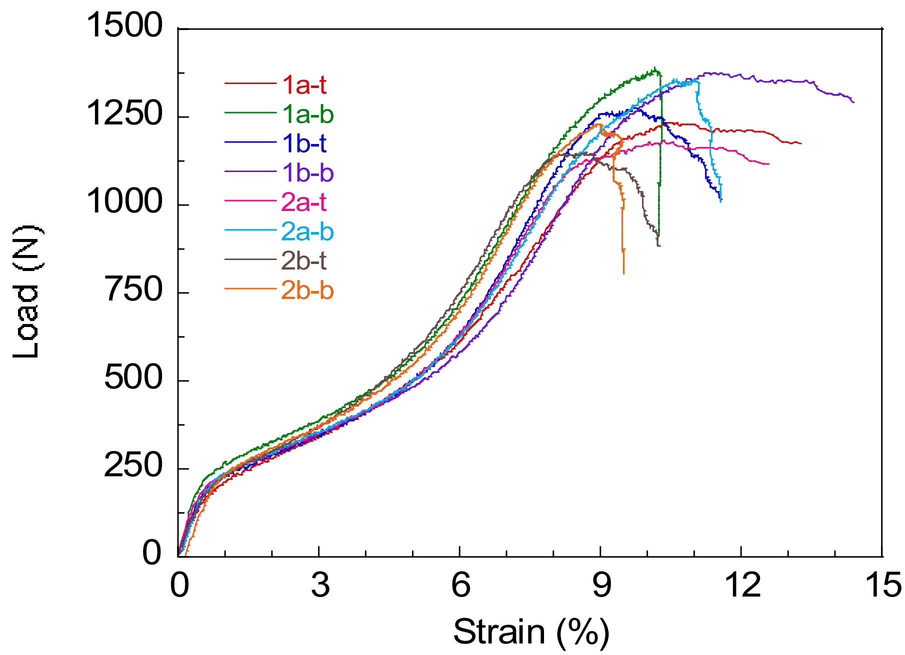

Figure 6. Collection of load versus strain curves obtained from tensile evaluation of recuperator strips.

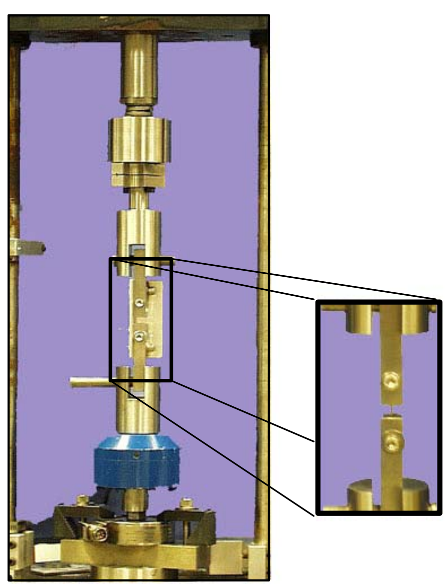

Figure 7. Experimental setup for the evaluation of miniature tensile specimens.

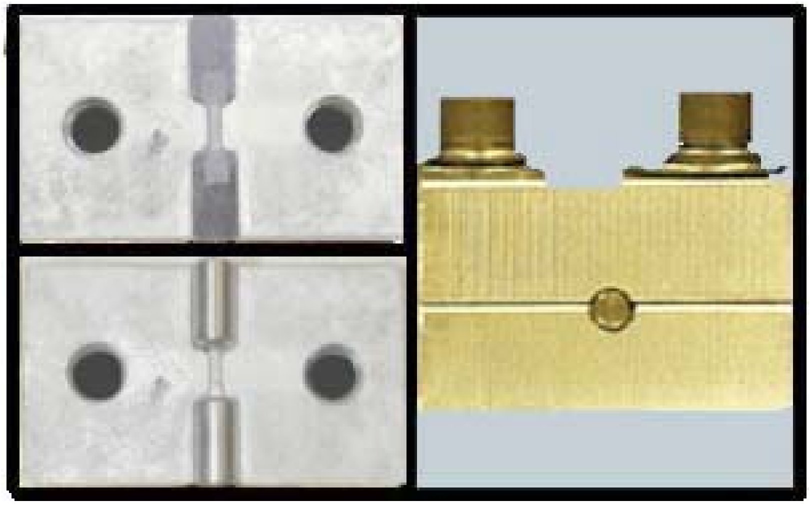

Figure 8. Miniature alignment fixture. The top portion of the fixture is used to keep the specimen and the end tabs aligned as well as to apply pressure to promote adhesion between the specimen and end-tabs.

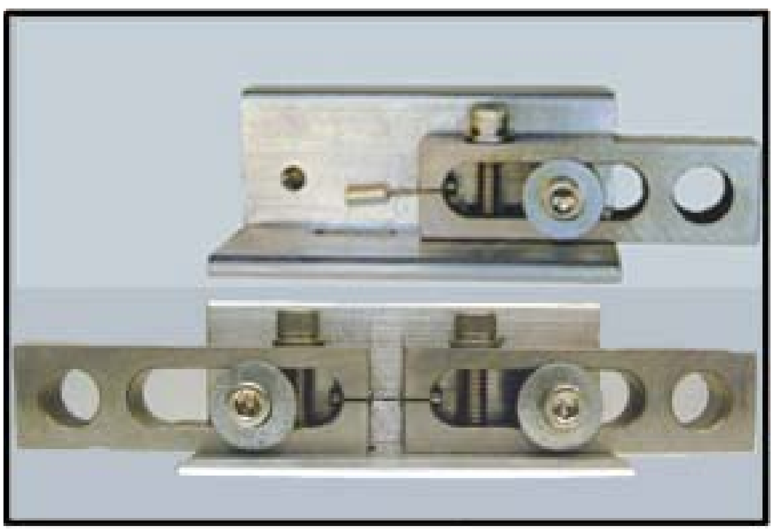

Figure 9. Mounting fixture for miniature tensile specimens.

Figures 10-12 show a collection of stress versus displacement curves for alloys HR-120, HR-230 and Haynes 214. These curves exhibit a liner region, associated with elastic behavior and a well-defined transition into plastic deformation. Table 1 summarizes the tensile strength results.

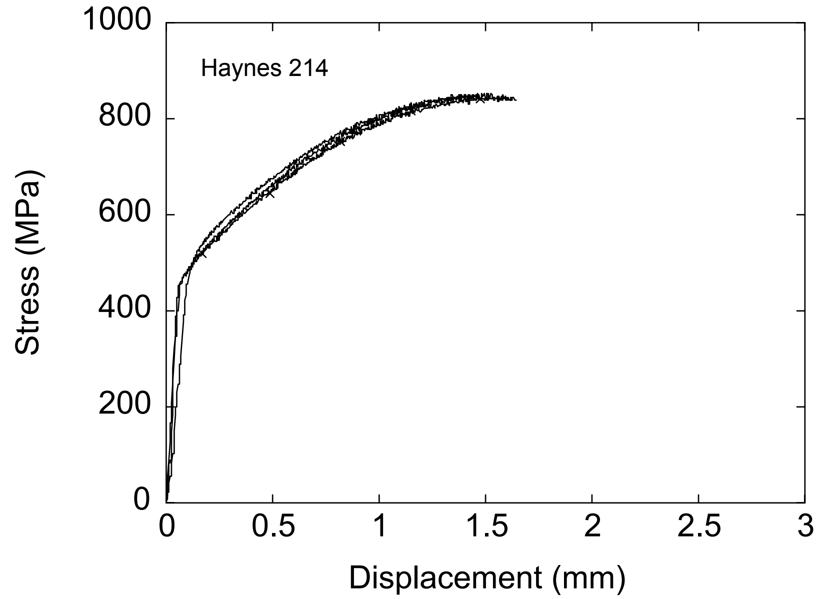

Figure 10. Stress versus displacement curves obtained from the tensile evaluation of Haynes 214 miniature tensile specimens.

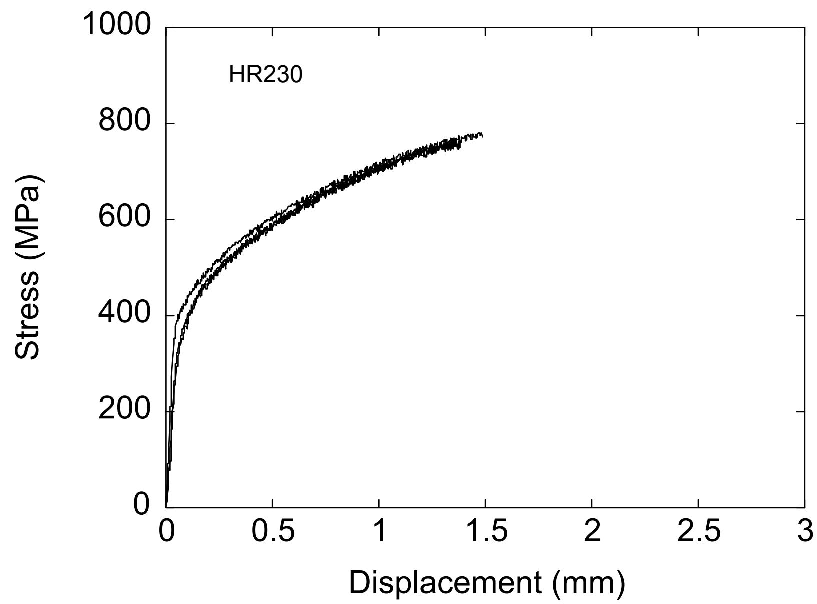

Figure 11. Stress versus displacement curves obtained from the tensile evaluation of alloy HR 230 miniature tensile specimens.

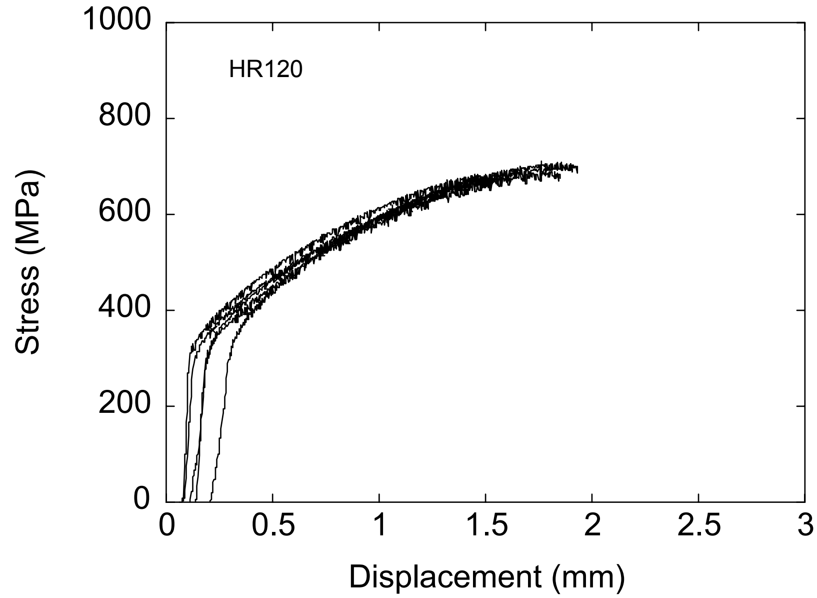

Figure 12. Stress versus displacement curves obtained from the tensile evaluation of alloy HR120 miniature tensile specimens.

Table 1. Summary of properties obtained from evaluation of miniature tensile specimens. Second set of numbers refers to thickness in thousands of an inch. Last character referts to longitudinal (v) or transverse (s)

Material	Average UTS (MPa)	Standard Deviation (MPa)
347SS-3.0s	717.30	7.41
347SS-3.0v	769.98	7.35
HR120-3.5s	689.17	11.87
HR120-3.5v	691.42	3.45
HR214-3.5s	851.96	2.31
HR214-3.5v	866.61	25.08
HR230-3.5s	778.57	15.79
HR230-3.5v	769.64	11.06
HR230-4.0s	816.59	12.55
HR230-4.0v	836.34	13.56

Status of Milestones

On schedule

Industry Interactions.

An agreement was established between UT-Battelle, LLC., the corporation that manages ORNL and CANMET of Canada to purchase two decommissioned Parallon 75 microturbines with recuperators and two recuperators for Parallon 75 microturbines. Negotiations had been started on September 2002, and the microturbines and recuperator were received at ORNL on March 8, 2003.

Problems encountered

None

Publications/Presentations

None